Effect of TiO_2 and ZrO_2 addition on phase evolution, densification and microstructure of Lithium Silicate ceramics

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Bachelor of Technology

By

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A journey is easier when you travel together. Interdependence is certainly more valuable than independence. This project is the result of five months of work whereby I have been accompanied and supported by many people. It is a pleasant aspect that I have now the opportunity to express our gratitude for all of them. I would like to express my deep and sincere gratitude to NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA.

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Lastly, I would like to thank my parents for being a strong support to me throughout this project and encourage me.

Dishu Bhatia

National Institute of Technology, Rourkela

CERTIFICATE

This is to certify that the thesis entitled, "**Effect of TiO_2 and ZrO_2 addition on phase evolution, densification and microstructure of Lithium Silicate ceramics**" submitted by Mr. **Dishu Bhatia** in partial fulfilments for the requirements for the award of **Bachelor of Technology** degree in **Ceramic Engineering** at National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/ Institute for the award of any Degree or Diploma.

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ABSTRACT

Lithium ortho-silicate (Li_4SiO_4) powder was synthesized using cheaper source of silica like rice husk ash through solid-state reaction of Li_2CO_3 (Lithium Carbonate) and SiO_2 (Silica). Phase pure powder could be produced at 800^0C calcined for 4h. In this report we studied the phase evolution, densification and corresponding microstructural properties in Li_4SiO_4 on the addition of TiO_2 and ZrO_2 nano powder by solid-state mixing process. The obtained powders are pressed and sintered at three different temperatures i.e. 900^0C, 950^0C, 1000^0C. The structural, microstructural and mechanical properties of above samples were investigated by X-ray Diffraction, Field Emission Scanning Electron Microscopy and Diametric Tensile Strength measurement respectively. It is observed that densification and diametric tensile strength (DTS) values of the Solid-state mixing of 1wt% nano TiO_2 and ZrO_2 to Li_4SiO_4 showed 76% and 81% of the theoretical density and DTS values of 3.9MPa and 4.1Mpa at 1000^0C, which is less than that of the pure Li_4SiO_4 samples.

CHAPTER 1

INTRODUCTION

1.1 Present Scenario

In the present world, economy relies on burning fossil fuels to produce affordable energy. But this energy is been using in large amount and is the increasing interest of the public. Conventional fuels like coal, oil have been using on regular days and excess use leading it to its depletion. Alternative energy source is the prominent interest that led the research communities to work towards this area. Nuclear Fusion, in which small nuclei combines to form a large nucleus which can result in release of large amount of energy. It can be the future resource of the energy and is been under research for safe and free source of energy on the earth. The fusion reactor would be first introduced by using Deuterium and tritium, the heavier isotopes of hydrogen. Deuterium is readily available while Tritium source is yet to be determined.

1.2 Tritium Breeding materials

The lithium containing ceramics are found to be tritium breeding material in fusion reactor. Various lithium based ceramics have been studied like Li_2O, $LiAlO_2$, Li_2TiO_3, Li_4SiO_4, and Li_2ZrO_3 so far for tritium breeding material [1][2]. Recently, Lithium ortho-silicates is one of the most prominent source of tritium with better properties like high Lithium atom density, high melting temperature and convenient tritium releasing behaviour.

1.3 Fusion Mechanism

Nuclear Fusion is the process in which merging of two light nuclei occurs and resulting in a heavier nuclei plus energy. This released energy is very high in amount as compared to current energy sources. Sun energy, on which we are totally dependent, is one of the best examples of fusion occurring naturally. Fusion reaction occurs when among the two positively charged nuclei, one has to overcome the long range Columbic forces in the field of other nuclei. Once the nuclei reach very close to other nuclei at which the strong short range nuclear forces become significant, the fusion reaction occurs.

$$ {}_1^2D + {}_1^3T \rightarrow {}_2^4He(3.5MeV) + n^0(14.1MeV) $$

Fusion Reaction of Deuterium and Tritium (isotopes of hydrogen)

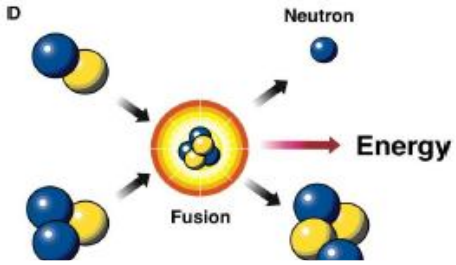

Fig.1 Nuclear Fusion

1.4 Why lithium is necessary for tritium breeding material

Lithium is found to be the only stable element to breed tritium in an easier way. Naturally occurring lithium consist of two stable isotopes, ^{6}Li and ^{7}Li, the latter being the more abundant. Atoms having low atomic numbers and a nucleus that contains different number of protons than neutrons usually drop to a lower energy state through mechanism of radioactive decay that causes similar number of protons and neutrons. ^{7}Li isotope of lithium contains an extra neutron in its atomic nuclei thus has a lower proton to neutron ratio which results into low binding energy. That's why Lithium is considered to be suitable for tritium breeding than any other element like helium or beryllium. Lithium is the stable light element.

1.5 Different types of lithium breeding materials

1.5.1 Lithium ortho-silicate(Li_4SiO_4)

Lithium orthosillicate is a compound composed of lithium and silicon elements. It is a good tritium releasing compound because of easy Lithium ion movement in its geometry, low activation, and chemical stability. The crystallization of Li_4SiO_4 is a monoclinic system. It is most commonly prepared by combination of Lithium Carbonate and Silica using solid-state method. Its density is found to be 2.40 gm. /cm^3 and has a melting temperature of 1533^0C [3]. It is used in various applications like Lithium Ion batteries etc. Lithium ortho-silicate (Li_4SiO_4) consist of good lithium atom density and shows the most viable tritium release behaviour as compared to other lithium based compound but it does not produce durable activated products during irradiation in fusion reactor.

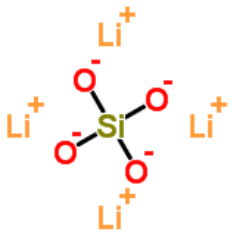

Fig. 2 Lithium Silicate Structure

1.5.2 Lithium Titanate (Li_2TiO_3)

Lithium titanate (Li_2TiO_3) has three different polymorphs. Stable polymorph is known as β-Li_2TiO_3. Other than this, another polymorph stable at high temperature is cubic phase called γ- Li_2TiO_3. Transition temperature from β-Li_2TiO_3 to γ- Li_2TiO_3 reversibly in the range of 1150^0C to 1250^0C [5]. A metastable phase is also formed in low temperature synthesis of Li_2TiO_3 which is called α-Li_2TiO_3. It transforms to stable β- Li_2TiO_3 at temperature around 400^0C [6]. It is also known for its good tritium releasing behaviour. Lithium Titanate (Li_2TiO_3) also has good tritium release properties but it is low activated material. It has a better thermal conductivity than other materials like Li_4SiO_4. It has high thermal and chemical stability, mechanical resistance as compared to other breeding materials. Sensitivity to moisture is very less compared to other breeder ceramic material.

1.5.3 Lithium Zirconate (Li_2ZrO_3)

Lithium Zirconate (Li_2ZrO_3) has its various applications in the electrochemical field, since it is both an ionic conductor and is thermodynamically stable against Li. Moreover, it is considered as a strong source for tritium breeding compound in fusion reactor. The XRD of Li_2ZrO_3 can locate only the Zr and O atoms. Later, using neutron profile refinement, Li ions were located in it. It is also a good tritium releasing behaviour but not good as Li_4SiO_4 and Li_2TiO_3 also in terms of activation [7]. Activation of zirconium is a tough task. It also shows problem in tritium retention at low temperatures. Stability of Li_2ZrO_3 is better than other ternaries (Li_4SiO_4 and Li_2TiO_3)[8]. Li_2ZrO_3 has high radioactive characteristics [9].

In summary, lithium silicate and lithium titanate are genuine low-activation materials. Lithium silicate was poor in density and lithium metatitanate shows superior mechanical properties compared to lithium Orthosillicate. Hence, it is anticipated that combination of these two materials will give a breeder material with improved mechanical properties, without losing the benefit of the good tritium release. The addition of titania (TiO_2), zirconia (ZrO_2) may modify the properties of the lithium orthosilicate system.

CHAPTER 2

Literature Review

2.1 Phase study of Li_2O-SiO_2 system

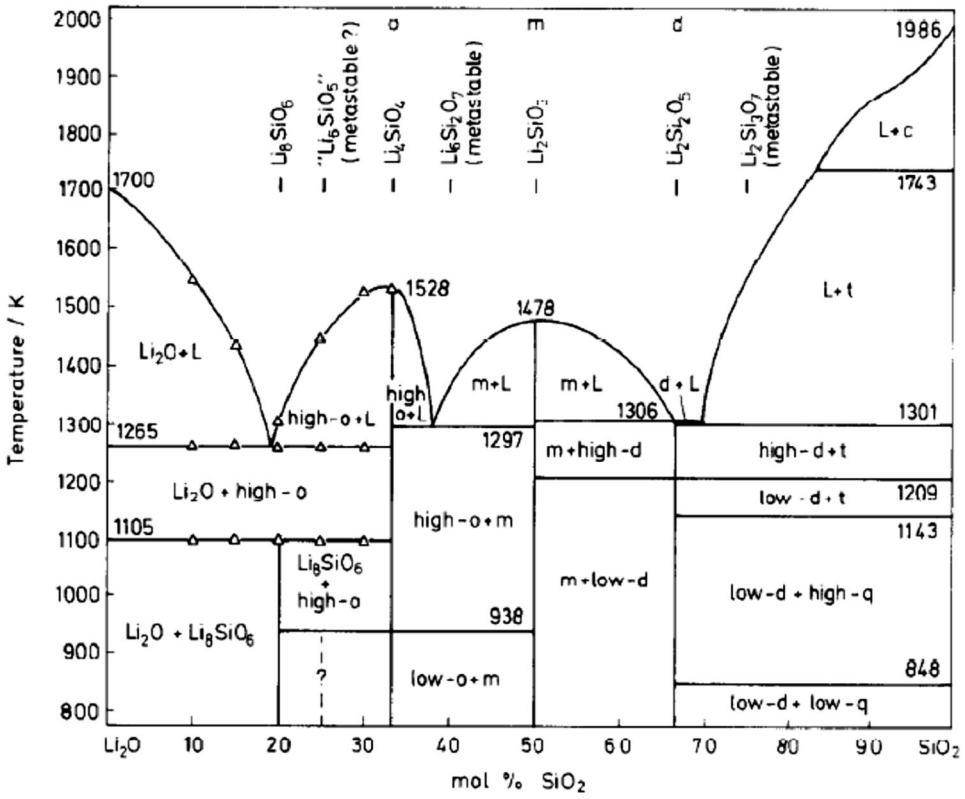

Fig. 3 Phase diagram of the Li_2O-SiO_2 system

Kracek et al[10] was the first who studied the equilibrium diagram of Li_2O-SiO_2 system. By examining the above phase diagram of Li_2O and SiO_2 system which contains 0 – 100 mol% SiO_2 and Li_2O it is seen that three distinct phases of lithium silicates like Li_4SiO_4, Li_2SiO_3 and $Li_2Si_2O_5$ are seen with 33.3 mol%, 50 mol% and 66.67 mol% of SiO_2 respectively. Liquid phase of Li_2O is formed below 20 mol% SiO_2 and temperature above 1265K. Li_4SiO_4 and Li_2SiO_3 forms eutectic point at 1297K. For SiO_2 concentration below or above 33.3 mol%, it always exist in a liquid phase. It is also observed that Li_4SiO_4 decomposes into its constituent before its melting point is reached at 1528K with the concentration of 33.3 mol % SiO_2.

2.2 Crystallinity of Lithium Ortho-silicate

Völlenkle et al[11], were the first to study the crystal structure of Li_4SiO_4. According to them, Li_4SiO_4 having monoclinic structure with dimensions of unit cell as a =5.14Å, b = 6.10Å, c = 5.30Å and β = 90.5^o and space group *P21/m*. The six different Li atoms are found in this

monoclinic structure in which all lithium sites are partially filled ranging from 1/3 to 2/3 occupancy factor.

Tranqui et al[12] examined the crystal structure of Li_4SiO_4 and determined the unit cell of Li_4SiO_4 as a 'superstructure' that was formulated of 14 formula units, which was seven times larger than the structure reported by *Völlenkle et al*[11]. It also had monoclinic geometry but the dimensions of unit cell were a = 11.546 Å, b = 6.09Å, c = 16.645Å and β = 90.5o and space group *P21/m*. The differences in the unit cell parameters of Li_4SiO_4 was mainly because of the ordered structure.

Munakata et al[13] observed the electron state of Li_4SiO_4 crystal. According to this theory, the Li_4SiO_4 was composed of SiO_4 of tetrahedral geometry with Li atoms moving around them. This crystal structure of Li_4SiO_4 had 126 atoms (14 Si, 56 O and 56 Li) per unit cell.

2.3 Synthesis of Li_4SiO_4 by various processes

Pfeifer et al[14] synthesized Li_4SiO_4 powders via solid state, precipitation and sol-gel methods. They used amorphous silica gel and TEOS as the source of silica. They produced phase pure Li_4SiO_4 powders using solid state method when calcined at 900^oC for 4 hrs. Non-homogenous polyhedral crystals with large particle size (~50µm) and low surface area (0.6m2/gm) powders are obtained. The powder prepared by all the above routes showed low surface area irrespective of the synthesis route followed.

Tao Tang et al[15] prepared Li_4SiO_4 powders through solid state technique using amorphous silica as silica source. The Lithium silicate powders were synthesized at 700, 800 and 900$^\circ C$ with Li:Si molar ratios of 0.5, 1, 2 and4, respectively. For Li: Si , 0.5, 1 and 2 at 700^0C, the major crystalline phase is Li_2SiO_3 and it increases with increase in Li/Si molar ratio. Pure Li_2SiO_3 can be obtained at 900^0C when Li/Si is equal to 1. For Li/Si equal to 4, Li_4SiO_4 with purity 98% is obtained at 700^0C and phase pure powders can be produced by calcining at 800^oC for 4hrs.

Chang et al[16] followed a solution based wet chemistry approach for the preparation of Li_4SiO_4. And they utilized fumed silica with high specific surface area (~350m^2/gm). Two different source of lithium has been used viz lithium nitrate and lithium hydroxide. The homogenously mixed solution of $LiNO_3$/LiOH and silica were then subjected to

rotary evaporation at a pressure of 600 Mbar at 140°C for 1 h, followed by a pressure of 100 Mbar at the same temperature for 2 h. The Li_4SiO_4 phase evolution was changed with change in Li-source and it begins to evolve Li_4SiO_4 phase at 500°C and 600°C when the as-prepared powders generated from $LiOH.H_2O$ and $LiNO_3$ respectively.

Wu et al [17] utilized aerosol silica as the silica source for the synthesis of Li_4SiO_4 along with hydrated LiOH. They followed the water based sol-gel method in which citric acid is used as a Chelating agent. Phase pure Li_4SiO_4 is produced at 675°C. Powder characterization techniques like BET surface area and SEM was done. This sol-gel derived powder has better sinterability over solid state derived powder.

Cruz et al[18] used silicic acid (H_2SiO_3) as the source of silica for synthesizing Li_4SiO_4 through modified solid-state combustion technique. Lithium hydroxide and Urea considered as the precursors in this process. They have varied the molar ratio of the reactants from 2:1:3 to 7:1:3 and heating temperature of the furnace from 450°C to 1100°C. Phase analysis of the obtained powders reveals different lithium silicate compounds like Li_2SiO_3, $Li_2Si_2O_5$, and Li_4SiO_4 at different molar ratios. It is found that highest percentage (~98%) of Li_4SiO_4 along with minor quantities of Li_2CO_3 is obtained with 6:1:3 molar ratio of LiOH: H_2SiO_3: CH_4N_2O at 1100°C.

Choudhary et al[19] synthesized phase pure lithium orthosilicate (Li_4SiO_4) by the solution – combustion technique as well as solid state method using rice husk ash (RHA) as silica source. It was found that by controlling the metal to citrate ratio of the starting solution, phase pure powder can be prepared at 650°C.Whereas in solid state method, calcination at 800°C was required to achieve phase purity. The particle size of Li_4SiO_4powder (prepared at C/M = 1.4) was found to be 100–200 nm. They achieved 83% of the theoretical density at a temperature as low as 900°C.

2.4 Densification behaviour of Li_4SiO_4

Lithium compounds suffer from volatilization of lithium at low temperature and thus sintering of ceramics is difficult. Achieving 80% of the theoretical density could be a difficult task by maintaining Li_4SiO_4 phase.

Wu et al[17]stated the sintering behaviour of Li_4SiO_4 and found that linear shrinkage of 5.2% occurred prepared by sol-gel method at 915^oC. Density of 82.9% of RD was obtained at 1000^oC/4hrs.

Cruz et al[18] studied the kinetics and the thermal stability of lithium silicates. According to this theory, Li_4SiO_4 gets converted to Li_2SiO_3 between 900^oC and 1000^oC. It happens because of the Li_2O sublimation. After the sublimation of Li_2O, the tetrahedrons of Li_4SiO_4 modify themselves to produce chain structure of Li_2SiO_3.

R. Knitter et al[20] prepared Li_4SiO_4 samples with addition of Titania to improve the mechanical strength of the sintered ceramic. The prepared samples having 5–20mol% lithium metatitanate as a secondary phase besides lithium orthosilicate. They found that the melting temperature was decreased with increase in titanate content and down to about 1473 K for a composition with 20 mol% metatitanate, compared to the melting temperature of pure lithium orthosilicate of 1531 K.

2.5 Objective

Our objective is to prepare Li_4SiO_4 dense ceramic by in-situ formation of Li_2TiO_3 and Li_2ZrO_3 phases without much degrading its Li-atom density. Our other objectives are to study the phase evolution, densification and microstructure of Li_4SiO_4 ceramic on the addition of nano TiO_2 and ZrO_2. The above objectives can be fulfilled by taking following steps.

- ✓ Preparation of Amorphous silica from Rice husk.
- ✓ Synthesis of Phase pure Li_4SiO_4 powder using cheaper silica source Rice husk.
- ✓ Phase and particle size analysis of the synthesized powders.
- ✓ Preparation of Li_4SiO_4 –TiO_2 and Li_4SiO_4-ZrO_2 samples using solid-state mixing method.
- ✓ To study the phase and densification behaviour of Li_4SiO_4 sintered samples on the addition of TiO_2 and ZrO_2.
- ✓ Microstructural analysis of the sintered pellets.
- ✓ To study the mechanical strength of the sintered ceramic.

CHAPTER 3

Experimental Work

3. Experimental Work

3.1 Preparation of Silica by Rice Husk Ash Method

The preparation of silica from Rice Husk involves following steps: washing, leaching, drying and firing. The Rice husk collected from local rice mill was washed properly with tap water to remove unwanted fine dust materials and the physically adhered impurities. After washing, husk was kept it under sunlight or IR lamp for drying. The cleaned husk was acid leached using 3 N HCl (Merck, India) solutions with simultaneous heating for 1 h. Now the leached husk was washed with warm water continuously to remove acid. The leached husk was then dried and Fired at 700^{o}C for 6 h in air atmosphere to get the silica whiskers. The obtained silica whiskers were then pot milled for 6hrs using iso-propyl alcohol (IPA) and 10 mm zirconia balls. After milling the solution (IPA + Rice husk ash) was dried for 4hrs in an air oven. Fig shows the flow diagram of extraction of silica from Rice husk.

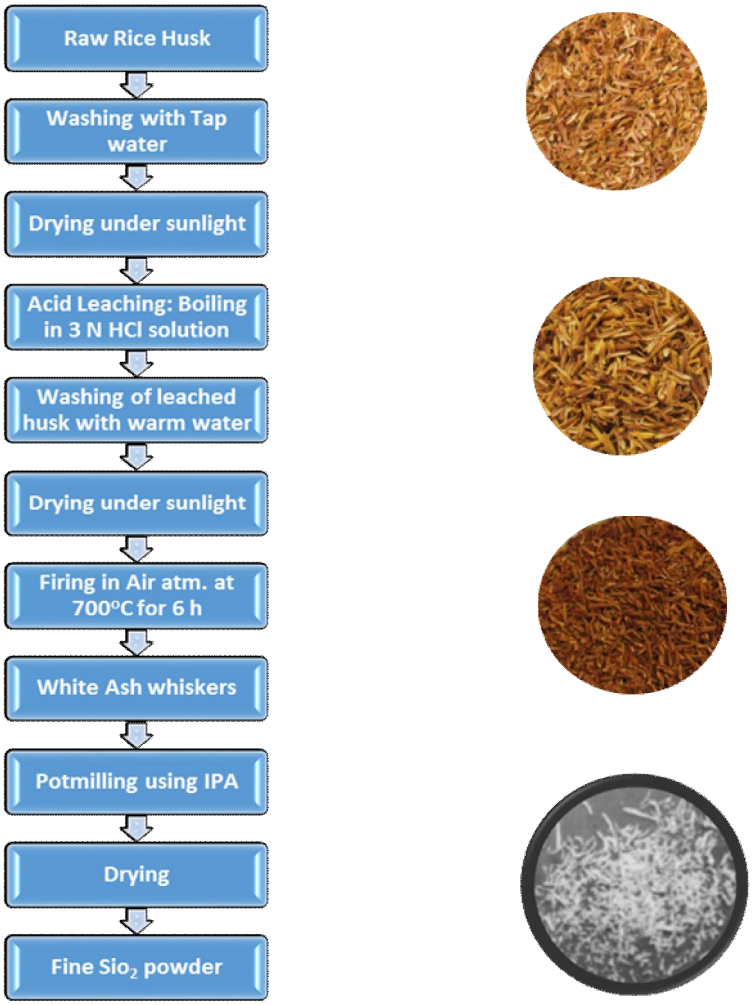

Fig. 4 Flow Chart and pictures for preparation of silica from RHA

3.2 Preparation of Lithium orthosillicate using silica from RHA

Li_4SiO_4 powder was prepared through solid state technique using silica from RHA route as silica source. Stoichiometric mixture of Li_2CO_3 (Merk, Germany) and SiO_2 was taken into a container along with 10mm zirconia balls in a proper ratio. This mixture was pot milled for 6hrs using 2-Propanol (Merk, India) as milling medium Now milled mixture was dried at 100^oC in an oven for 2hrs then calcined in a chamber furnace at 800^0C for 4hrs in air atmosphere. The possible reaction during calcination was as follows

$$2\ Li_2CO_3 + SiO_2 \longrightarrow Li_4SiO_4 + 2\ CO_2$$

3.3 Addition of TiO_2 and ZrO_2 to Li_4SiO_4 powder prepared by solid state method

1, 3 and 5 wt% of nano TiO_2 and ZrO_2 powder of the considered batch was added to Li_4SiO_4 powder and pot milled for 6hrs. Now, the powders are kept for drying at 100^oC in an oven for 2hrs. The obtained powders grounded by using mortar and pestle along with the addition of 1wt% PVA and then pressed into pellets using 12mm die-punch. Now these pellets are kept for drying for 6hrs. These pellets sintered at 900^0C, 950^0C and 1000^0C in air atmosphere. The entire procedure was described in the following flow chart

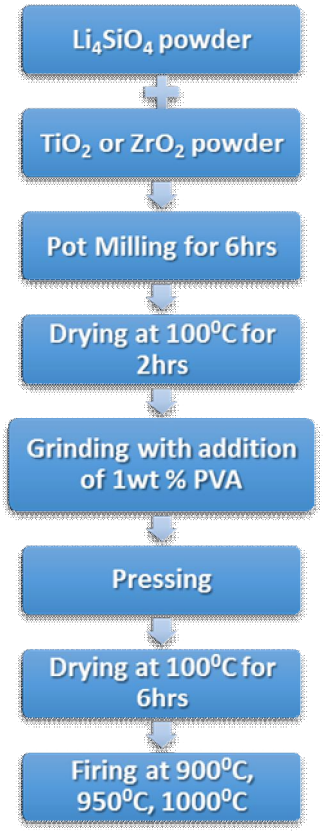

Fig. 5 Flow chart depicting fabrication of Li_4SiO_4 pallets added with TiO_2/ZrO_2 nano powder

3.4 Characterization techniques

3.3.1 Phase and microstructure analysis

The crystallization and the phase evolution of the calcined powders and sintered pellets were studied by X- Ray Diffraction Technique (Rigaku, Japan). Scanning of samples was done between 2Θ ranges 15 to 80^{o} range in continuous scan mode with 20 deg/sec scan rate. Phases present in the samples was identified by the search-match facility available with Philips X`Pert High Score Software. Microstructural and compositional analysis was done using FESEM (Field Emission Scanning Electron Microscope, Nova Nano SEM/FEI).

3.3.2 Particle size analysis

Laser diffraction method with a dynamic light scattering (DLS) technique was used to determine the particle size distribution of the powder. The Li_4SiO_4 powder was dispersed in acetone and measured the particle size using ZETA Sizer (Malvern Instruments Nano ZS).

3.3.3 Density Measurement

The Bulk density of the sintered pellets was calculated using the formula,

B.D. = Dry Weight/ Soaked Weight – Suspended Weight

Bulk density study of the sintered samples were done by Archimedes principle, using vacuum method in Kerosene medium (sp, gr. 0.81715).

3.3.4 Measurement of diametric strength

Diametric Tensile Strength of the sintered pellets was calculated using the machine namely **Tinius Olsen H10KS.** In this technique, a tensile load is applied on pallets and then DTS is measured by using formulae:

$$\mathbf{DTS = (2P)/(3.14*d*t)}$$

Where, P = load applied

d = diameter of the sintered pellet

t = thickness of the sintered pellet

CHAPTER 4

RESULTS & DISCUSSION

4.1 Characterization of Li_4SiO_4 powder

4.1.1 Phase analysis of Li_4SiO_4 powder

Fig.6 shows the XRD pattern of the phase pure Li_4SiO_4 powder prepared through solid-state reaction. The powders are calcined at 800°C for 4h. The XRD pattern shows the Li_4SiO_4 without any secondary phase.

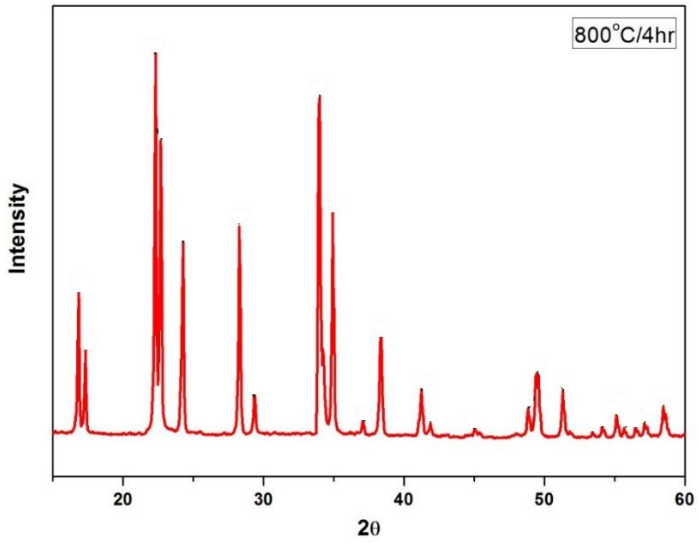

Fig. 6 XRD analysis of Li_4SiO_4 powder calcined at 800^0C

4.1.2 Particle Size Distribution of Li_4SiO_4 powder

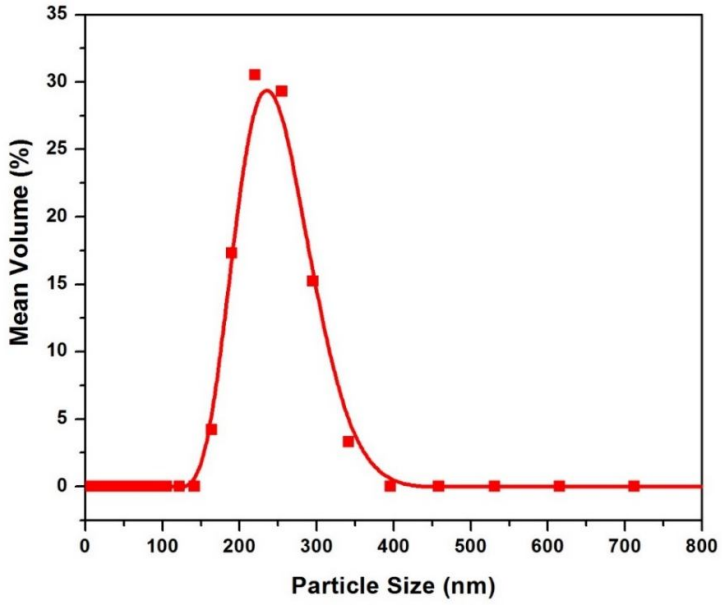

Fig. 7 Particle Size Distribution of Li_4SiO_4 powder calcined at 800^0C

Fig.7 shows the particle size distribution vs mean volume graph of Li_4SiO_4 powder dispersed in water. From the above graph it is found that maximum volume fraction about 97% having particle size in the range between 164nm to 295nm with an average particle size of 240nm.

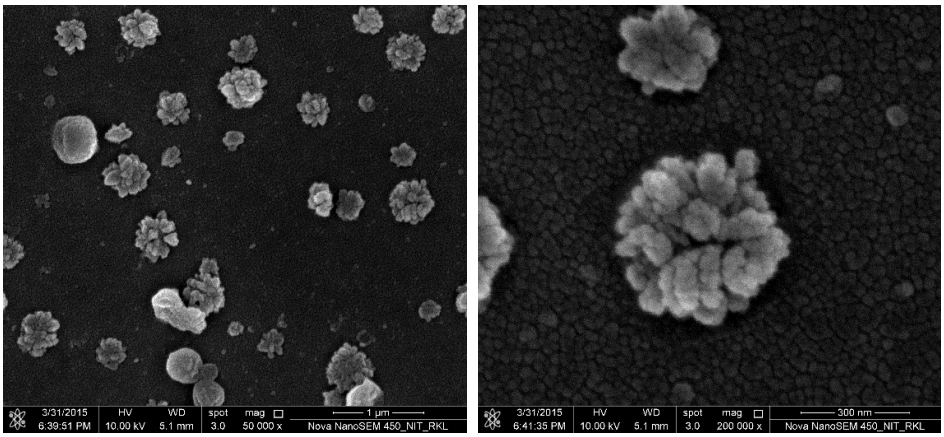

Fig 8 Microstructure of Li_4SiO_4 powder calcined at 800^0C

Fig.9 shows the FESEM images of Li_4SiO_4 powders calcined at 800^oC using solid state method. The obtained powders are dispersed in acetone for 30 min and the dispersed sample was dried on a glass slide. It is observed that Li_4SiO_4 powder has particle size in the nano size and forming agglomerates in the size of 200-500nm.

4.2 Sintering of Li_4SiO_4 powder with addition of TiO_2 and ZrO_2

Li_4SiO_4 powders prepared through solid state technique with the addition of 0, 1, 3, 5 wt% of Nano TiO_2 and ZrO_2 were sintered at the temperatures 900^o, 950^o and 1000^oC. The sintered samples showing decrease in density with increase in wt% of TiO_2 and ZrO_2 addition.

4.2.1 Phase analysis of the sintered pellets

Fig.9 and 10 shows the X-Ray Diffraction pattern of sintered pellets with the addition of 0, 1, 3 and 5 wt % of TiO_2 to Li_4SiO_4 powder and sintered at 900^0C and 1000^0C. XRD pattern reveals that no phase of Li_2TiO_3 was observed in 1wt% TiO_2 sample. On increasing the weight percent of TiO_2 significant amount of Li_2TiO_3 was formed in 3 and 5 wt% samples. And the intensity of the Li_2TiO_3 peak increases with increase in the amount of titania addition. Here, the Li_2TiO_3 phase was evolved at the expense of Li_4SiO_4 phase with a simultaneous formation of Li_2SiO_3.

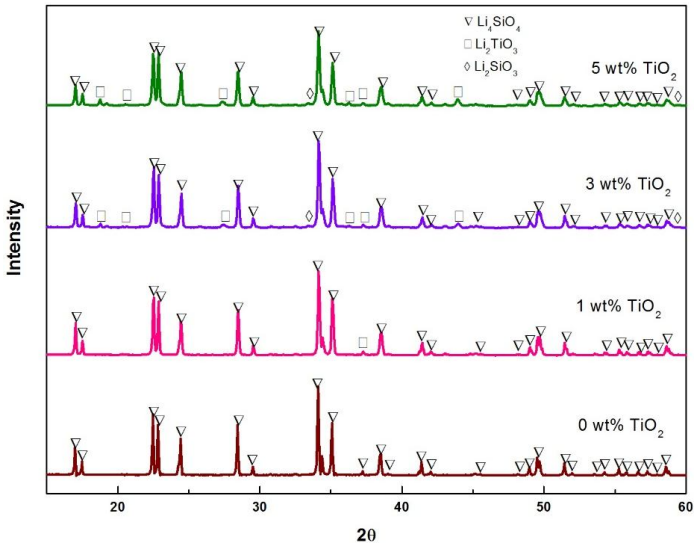

Fig. 9 XRD analysis of 0, 1, 3 and 5 wt% TiO_2 added Li_4SiO_4 sintered pellets at 900^0C

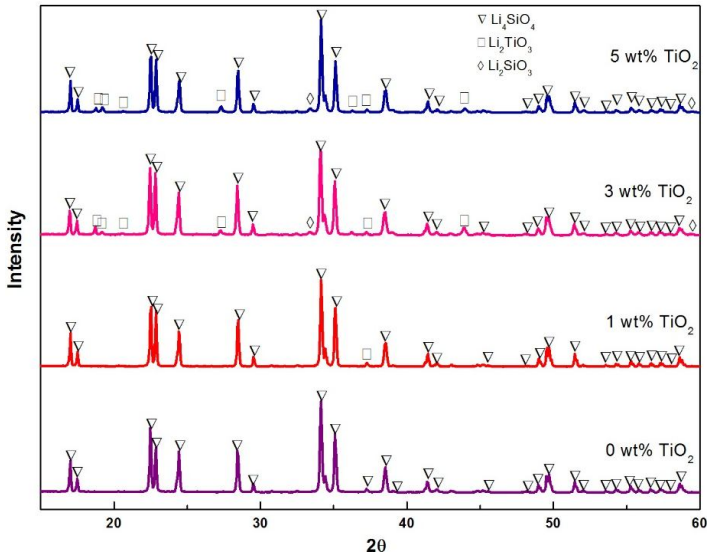

Fig. 10 XRD analysis of 0, 1, 3 and 5 wt% TiO_2 added Li_4SiO_4 sintered pellets at 1000^0C

Fig.11 and 12 shows the X-Ray Diffraction pattern of the sintered pellets with the addition of 0, 3 and 5 wt % of ZrO_2 to Li_4SiO_4 powder and sintered at 900^0C and 1000^0C. In case of 3 and 5wt% of ZrO_2 added samples significant amount of Li_2ZrO_3 was formed. The intensity of the Li_2ZrO_3 peak increases with increase in the amount of Zirconia addition. Here, the Li_2ZrO_3 phase was evolved at the Expense of Li_4SiO_4 phase with a simultaneous formation of Li_2SiO_3.

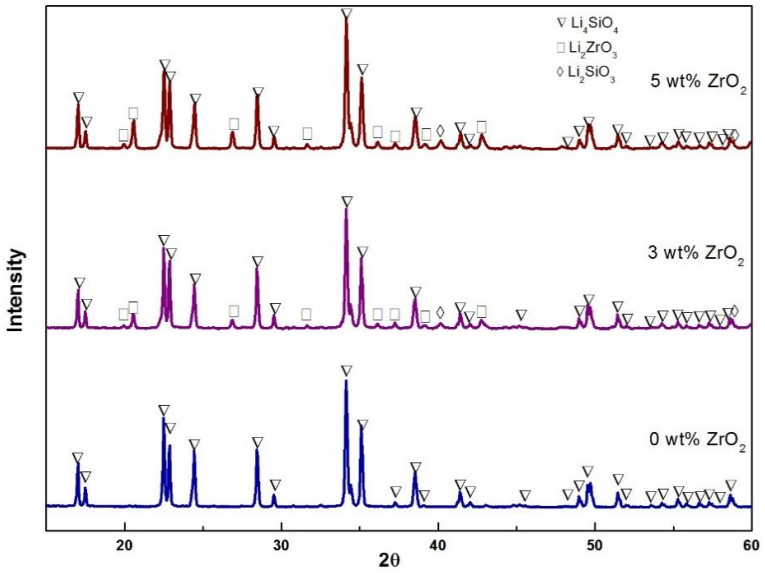

Fig. 11 XRD analysis of 0, 3 and 5 wt% ZrO_2 added Li_4SiO_4 sintered pellets at 900^0C

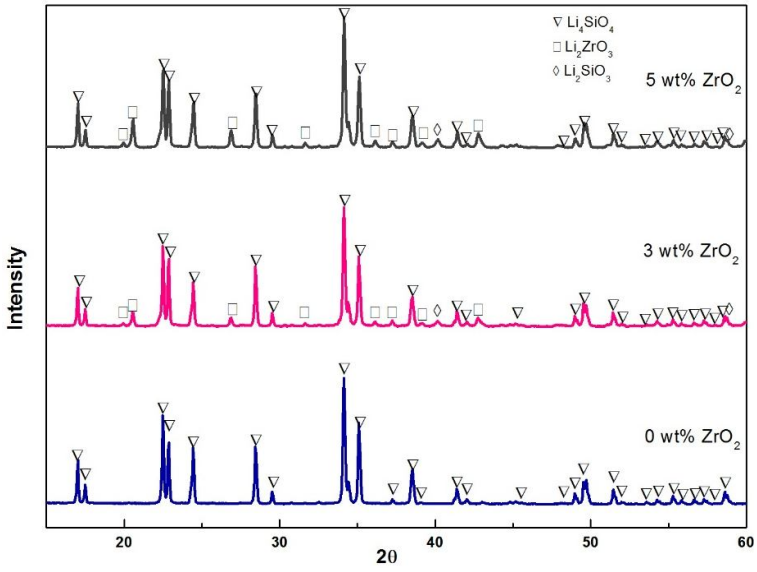

Fig. 12 XRD analysis of 0, 3 and 5 wt% ZrO_2 added Li_4SiO_4 sintered pellets at 1000^0C

4.2.2 Density measurement and Volume Shrinkage of sintered pellets

The volume shrinkage of the samples with the addition of 0, 1, 3, 5 wt% of nano TiO_2 and ZrO_2 as a function of sintering temperature was shown in Fig. 13 and 14. The volume shrinkage of the sintered pellets decreases with increase in the wt% of the nano additives. And for a particular composition the shrinkage increases with increase in temperature. This scenario was observed in both the cases i.e. addition of TiO_2 and ZrO_2. It is to be mentioned that high shrinkage with little improvement in density at higher temperature (950^oC and 1000^oC) indicates Li-evaporation from the system.

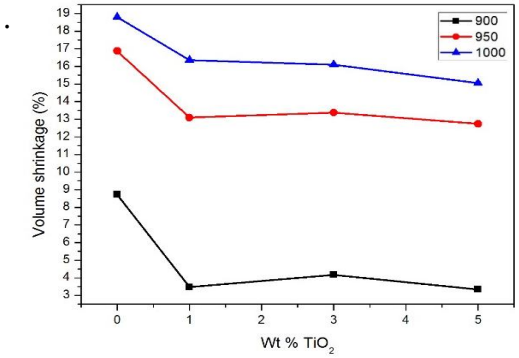

Fig. 13 Volume Shrinkage vs wt% of TiO_2 as a function of temperature

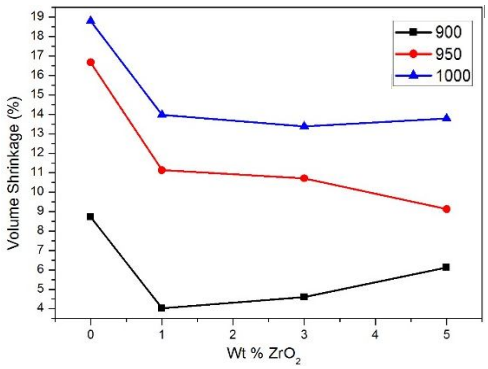

Fig. 14 Volume Shrinkage vs wt% of ZrO_2 as a function of temperature

Fig. 15 and 16 shows the variation of bulk density with increase in temperature as a function of temperature. The bulk density of the samples decreases with increase in wt% of the TiO_2 and ZrO_2. The density of the pure Li_4SiO_4 powder is higher than the powders with the addition of nano TiO_2 and ZrO_2. This may be due to the formation of Li_2SiO_3 which lowers the densification process in the system.

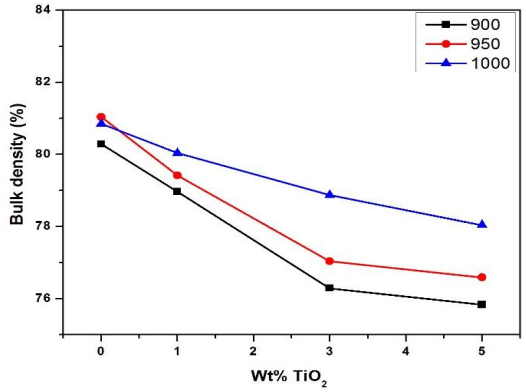

Fig. 15 Variation of Bulk Density with wt% of TiO_2

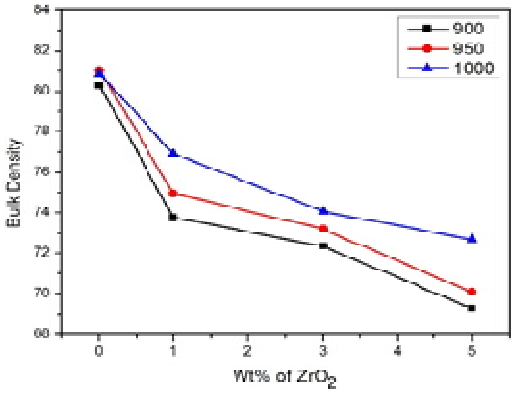

Fig. 16 Variation of Bulk Density with wt% of ZrO_2

4.2.3 Microstructural properties of Li_4SiO_4 sintered pellets

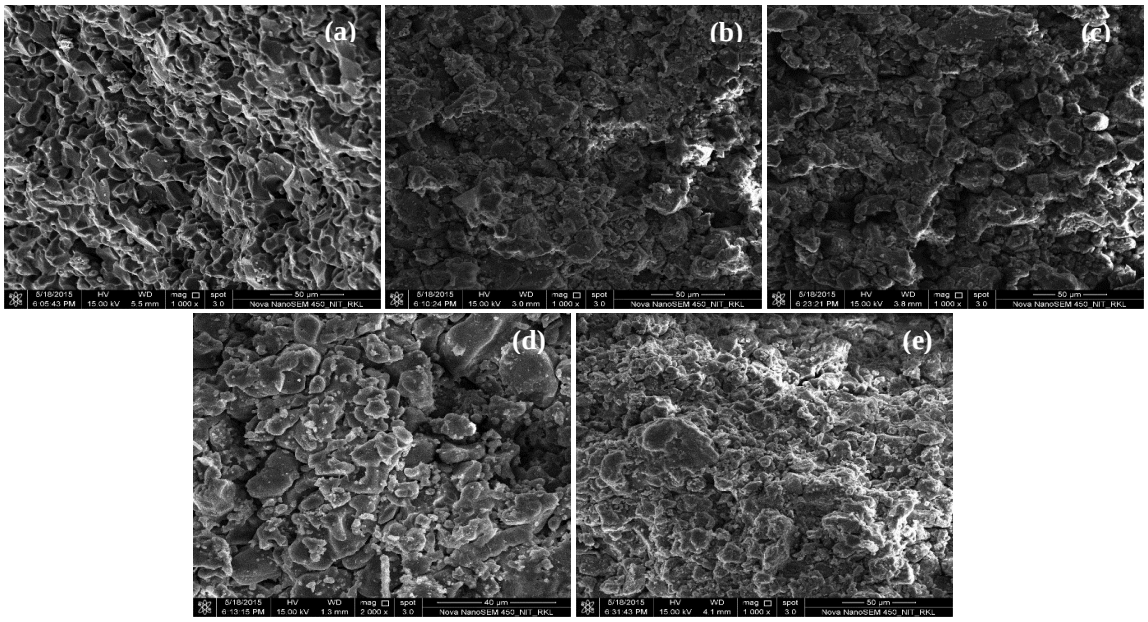

Fig 17. FESEM of TiO_2 added Li_4SiO_4 sintered pellets fractured surface (a) 0 wt%, 900°C, 3 wt% (b) 900°C, (c) 1000°C, 5 wt% (d) 900°C and (e) 1000°C

Fig. 17 shows the FESEM images of the sintered pellets at 900 and 1000°C. Fig 17 (a) is the fractured surface of the pure sample sintered at 900°C. Fig. 17(b), 17(c) and Fig. 17(d), 17(e) are the fractured micrographs of the 3wt%, 5wt% TiO_2 added pellets sintered at 900 and 1000°C respectively. Micro structure of 3wt% and 5wt% TiO_2 added samples showing a loose packing of grains that may be due to the presence of lithium metasilicate phase because of which the density of the samples decreases. The Li_2SiO_3 phase was also confirmed by XRD. With increase in the wt% of TiO_2 the density of the sample decreases as the Meta-silicate phase increases. Similar results were obtained in case of ZrO_2 added samples.

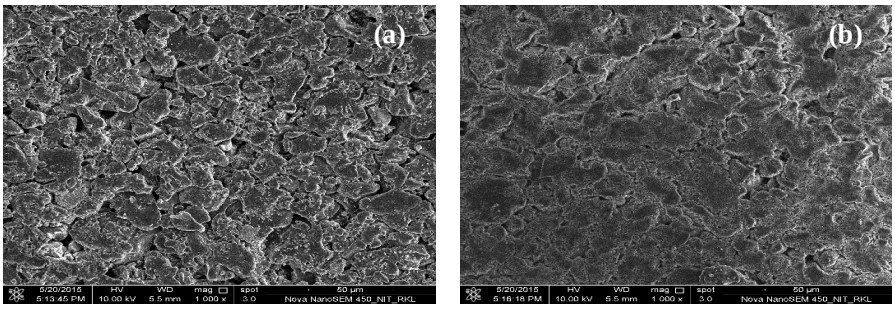

Fig. 18 FESEM of 5 wt% ZrO_2 added Li_4SiO_4 Pellets as fired surface sintered at (a) 900°C and (b) 1000°C

4.2.4 Measurement of Diametric Tensile Strength

Fig.19 and 20 shows the variation of Diametric Tensile Strength (DTS) of the sintered pellets at different temperatures as a function of wt% of TiO_2 and ZrO_2. DTS values are decreasing with increase in wt% of TiO_2 and ZrO_2 and it is increasing with increase in temperature for a particular composition. As a whole the modified Li_4SiO_4 samples showing poor mechanical properties than the pure sintered sample.

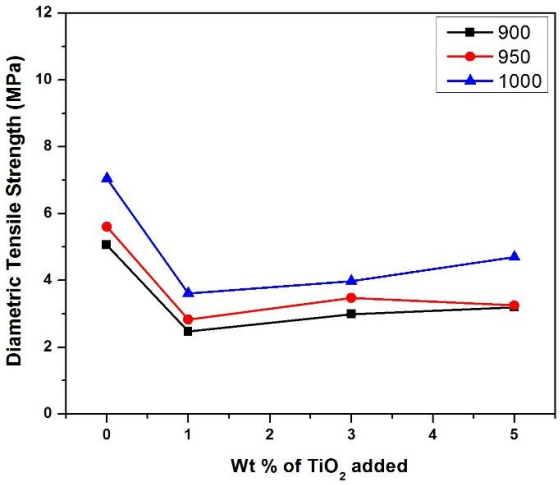

Fig. 19 Effect of wt% of TiO_2 on Diametric Tensile Strength of Li_4SiO_4

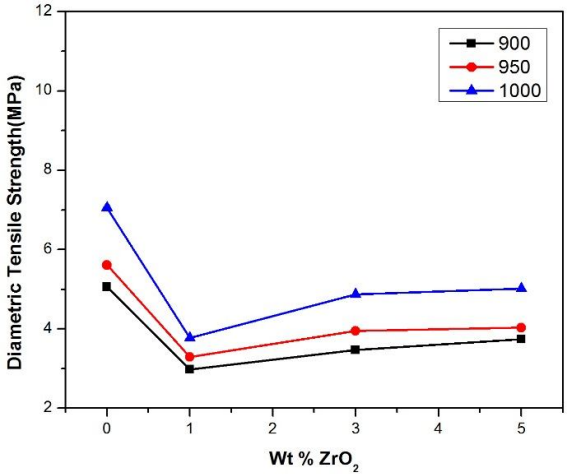

Fig. 20 Effect of wt% of ZrO_2 on Diametric Tensile Strength of Li_4SiO_4

5. Conclusions

- Amorphous SiO_2 with good purity was prepared from cheaper precursor like Rice husk.
- Phase pure powders could be produced at 800^oC using silica prepared from rice husk through solid-state process.
- Addition of nano TiO_2 and ZrO_2 to Li_4SiO_4 phase using solid-state mixing resulted in poor densification and mechanical strength (DTS) in the sintered specimens.
- This is due to the formation of Li_2SiO_3 as a secondary phase in sintered ceramics.
- In solid state mixing, densification and DTS values decreased as we increased the wt% of TiO_2 / ZrO_2 and increased on increasing the sintering temperature for a particular composition.
- Solid-state mixing of 1wt% nano TiO_2 and ZrO_2 to Li_4SiO_4 showed 76% and 81% of the theoretical density and DTS values of 3.9MPa and 4.1Mpa at 1000^0C, which is less than that of the pure Li_4SiO_4 samples.

6. References

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